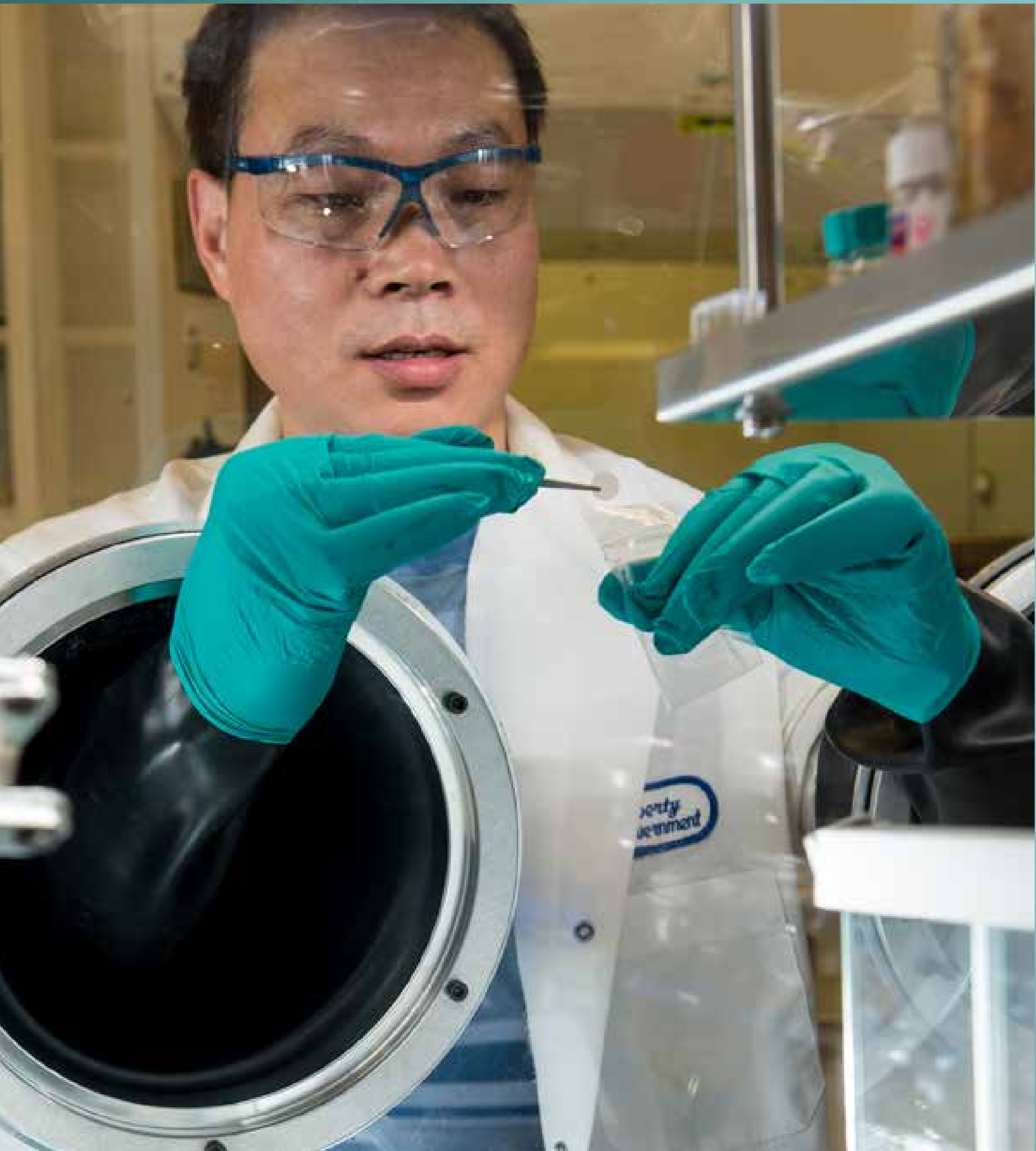
Customized **Nanoengineered Coatings** for Science and Industry



ARGONNE'S **ATOMIC LAYER DEPOSITION**

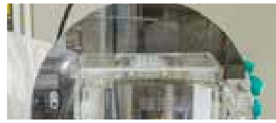
Argonne
NATIONAL LABORATORY

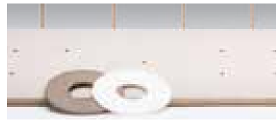
Argonne Offers Customized Nanoengineered Coatings and Equipment for Science and Industry

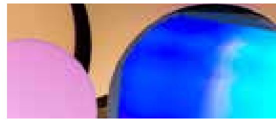
Argonne's advanced materials capabilities and intellectual property are available to scientific firms and industry. Argonne can create design-optimized solutions for materials manufacturing challenges that reduce costs, improve performance and increase the lifespan of materials.

Nanoengineered coatings have diverse applications in the manufacture of microelectronics, optics, sensors and solid-state detectors, to name a few. Of the many techniques for producing nanoengineered coatings, atomic layer deposition, or ALD, offers superlative performance. Argonne National Laboratory's award-winning, renowned materials scientists and engineers lead the world in the development and use of atomic layer deposition. Their exceptional capabilities in materials innovation and industrial processes, combined with the laboratory's unique, world-class facilities for materials characterization and analysis, enable game-changing advances in the state of the science and meet industry's need for new and customized nanoengineered coatings.

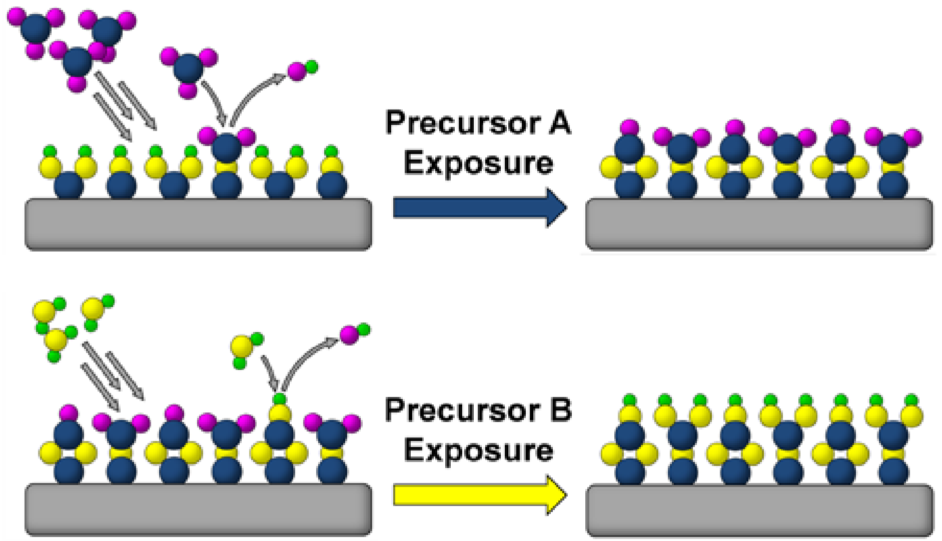
On the cover:
Argonne postdoctoral researcher Henry Meng assembles a prototype lithium battery incorporating ALD nanostructured materials.







Benefits of Atomic Layer Deposition



ALD uses sequential precursor exposures and self-limiting surface chemistry to produce atomic layer-by-layer growth

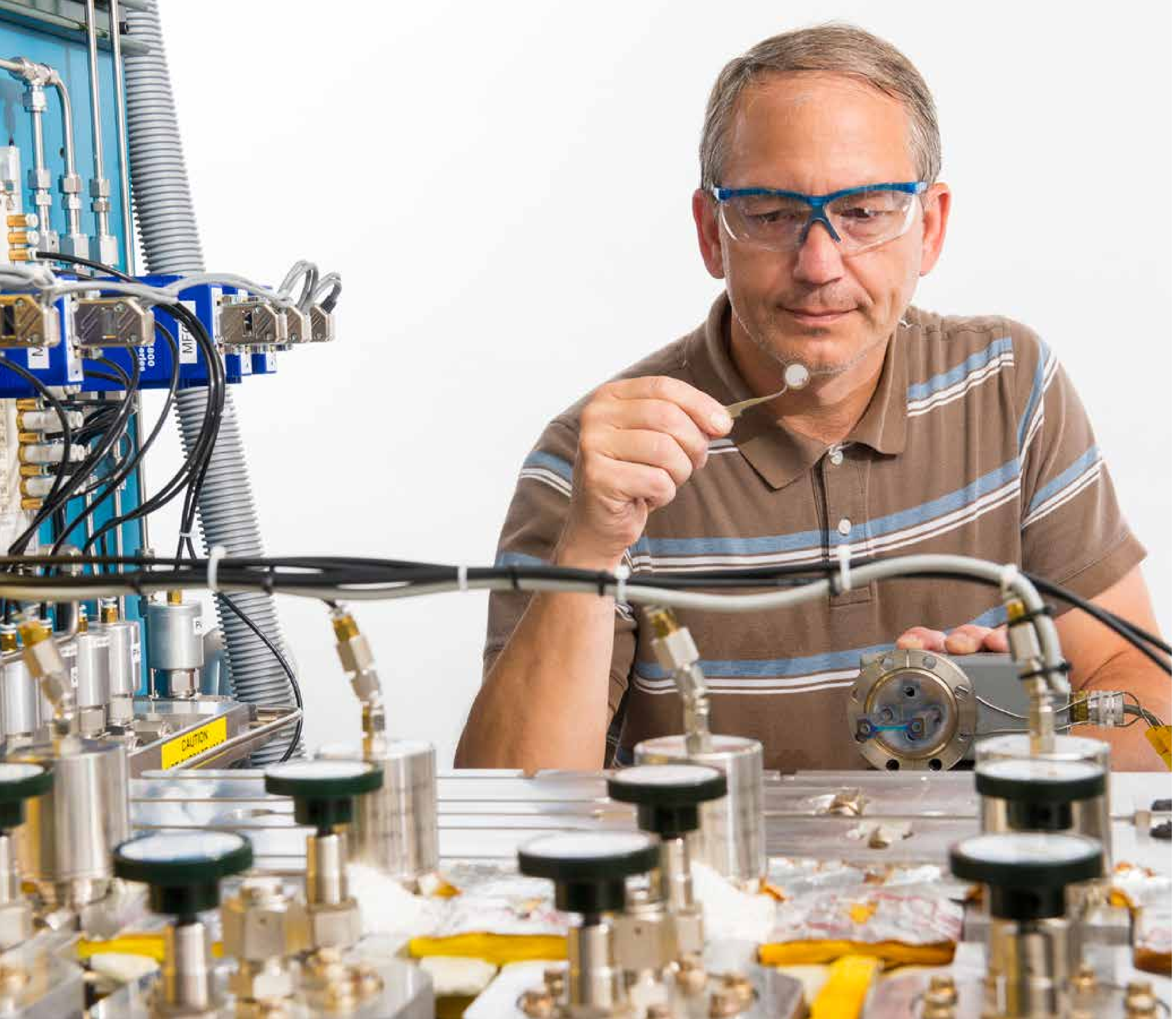
Array of "bubblers" containing chemical precursors used in atomic layer deposition.

Atomic Layer Deposition (ALD) is a highly controlled method for depositing precise thin films to a desired thickness onto a substrate. It enables the "growth" of differing multilayer structures.

In ALD, the gaseous precursors are individually exposed to a solid surface, allowing for a sequential atomic layer-by-layer process to occur. Because the chemical reactions taking place on the surface naturally terminate when the reactive surface sites are consumed, the amount of material deposited in one ALD cycle is easily controlled.

This self-limiting property, coupled with facile diffusion of the precursor vapors into narrow pores and voids, allows complex, three-dimensional substrates to be coated with excellent uniformity and conformity.

A rich variety of materials can be deposited by ALD including metal oxides, nitrides and sulfides, as well as pure elements. By alternating between the ALD chemistries for two materials (e.g., a metal and a metal oxide), nanocomposite coatings can be synthesized. The thickness of the coating is controlled by the total number of ALD cycles performed, and the composition is dictated by the ratio of the ALD cycles executed for the two ALD chemistries.



Novel Materials and Processes Dramatically Improve Manufacturing

The discovery and development of novel materials is enabling dramatic improvements in manufacturing for industries such as photovoltaics, catalysis and energy storage. Argonne's expertise in this area is unparalleled. Argonne's scientists and engineers employ atomic layer deposition to develop new nanophase materials whose properties are tailored specifically to meet the needs of industry. Examples of Argonne's many successes include nanocomposite charge drain coatings for electron-optical devices and carbon nanotube-metal sulfide nanophase materials for energy storage.

Argonne's success is due in part to its researchers use of a range of in situ characterization methods – including measurements at Argonne's Advanced Photon Source – to achieve a deeper understanding of the surface chemistry that is critical to all ALD processes. This lends greater predictive power in the development of better ALD materials and processes.

Argonne's advanced atomic layer deposition processes render the newly developed materials as thin films. For instance, three distinct "recipes" for depositing indium-tin oxide (a high-performance transparent conductor used in flat-panel displays) have been developed, each optimized to address a specific industry need – such as low temperature or high deposition rate. To accelerate the targeted process development, Argonne has also developed techniques for rapidly screening ALD precursors to identify the best precursor for a given task.

Argonne researcher Joe Libera inspects a nanoporous disc designed to enable in situ infrared measurements during ALD process development.

KEY INTELLECTUAL PROPERTY

"Markov Chain Solver for Ballistic Transport with Surface Chemistry," A. Yanguas-Gil and J.W. Elam, invention ANL-SF-13-072, Open Source.

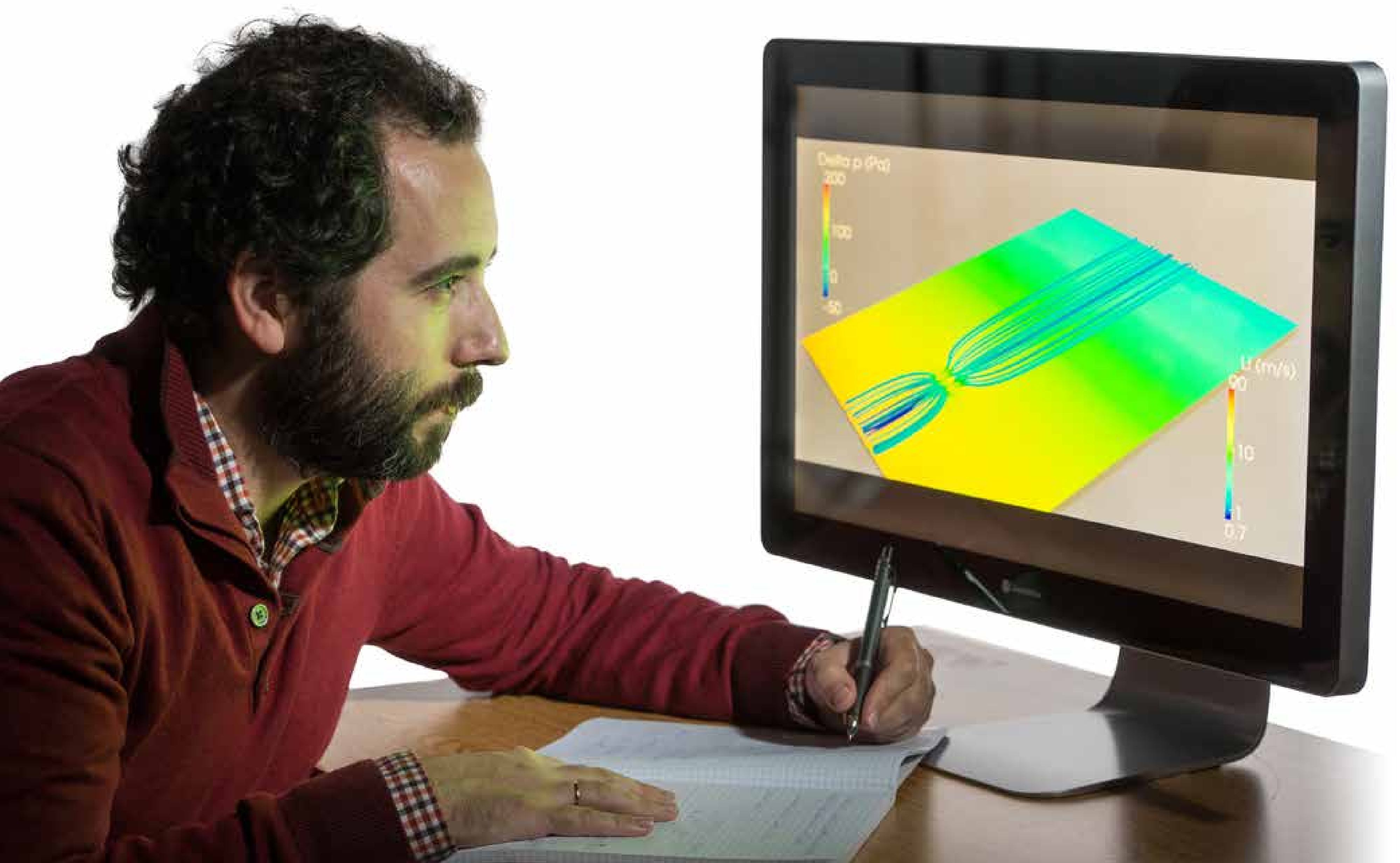
"Enhancement of Materials and Interface Performance of Materials via ALD Infiltration," A. Yanguas-Gil and J.W. Elam, invention ANL-IN-11-088, (2011).

"Deposition Control in Porous Substrates Using Surface Modification in Atomic Layer Deposition," A. Yanguas-Gil and J.W. Elam, invention ANL-IN-11-027, (2011).

"Growth Rate Control in ALD by Surface Functionalization," A. Yanguas-Gil and J.W. Elam, invention ANL-IN-10-028, U.S. Patent Application 2012/0213946 A1, published August 23, 2012.

"Spatially Controlled Atomic Layer Deposition in Porous Materials," J.W. Elam, J.A. Libera, M.J. Pellin and P.C. Stair, invention ANL-IN-07-079, U.S. Patent 8,318,248 B2 issued November 27, 2012.

Simulations Speed Development of Equipment for Large-scale Applications



Taking the atomic layer deposition technology from laboratory to use by industry demands that coatings be applied economically at large scales. Available commercial atomic layer deposition equipment that is designed primarily for coating silicon wafers for microelectronics is poorly suited for coating the large areas and porous materials required in emerging industries such as photovoltaics and energy storage. ALD equipment and processes are intimately coupled.

To address this problem, Argonne scientists are developing new ALD equipment that targets specific coating needs such as large substrates for photovoltaics, nanoporous granular media for catalysis and powders for lithium batteries. For this reason, Argonne's development of both new equipment and new ALD processes is a powerful asset for addressing the diverse needs of these emerging industries.

Developing specialized ALD coating tools can be time consuming and expensive. To accelerate this process, Argonne uses numerical simulation and modeling to evaluate design concepts prior to fabrication. However, the complexity of these new ALD tools can exceed the capabilities of existing software. Because of this, Argonne also develops novel software and analytical methods for performing these simulations. This new software allows the lab's researchers to simulate ALD chemistry over multiple length scales – encompassing the meter-sized reactor and also the nm-sized pores – to establish processing conditions that yield uniform coatings and maximize use of precursor.

Materials scientist Angel Yanguas-Gil uses Argonne's novel software and analytical methods to accelerate the development of atomic layer deposition coating tools for large-scale application processes.

KEY INTELLECTUAL PROPERTY

"Micro-Balance Sensor Integrated with Atomic Layer Deposition Chamber," A. Martinson, J.A. Libera, J.W. Elam and S. Riha, invention ANL-IN-11-094, U.S. Patent Application 13/591,498, filed August 22, 2012.

"ALD Reactor for Coating Porous Substrates," J.W. Elam, A.U. Mane and J.A. Libera, invention ANL-IN-12-036, U.S. Patent Applications 61/761,988 and 14/175,396 filed February 7, 2014.

"Method and System for Continuous Atomic Layer Deposition," A. Yanguas-Gil, J.W. Elam and J.A. Libera, invention ANL-IN-13-042, U.S. Patent Application 61/857,798 filed July 23, 2014.

Lower-cost Microchannel Plates for Sensing and Imaging

Argonne scientist Anil Mane holds a 12"-diameter silicon wafer coated with an ALD resistive film.

2012 R&D 100 Award Winner

Microchannel Plate (MCP) detectors are used in a wide variety of advanced imaging and sensing applications ranging from medicine and physics to national security. MCPs identify low levels of electrons, ions, photons or neutrons; they provide a greatly amplified "image" of the input signal. In medicine, imaging cameras such as Positron Emission Tomography scanners help doctors to provide early and accurate detection of the onset and progression of diseases. For national security purposes, flat-panel neutron detectors could be used to screen shipping containers or trucks for nuclear materials. In the scientific community, particle detectors are essential to advancing large-scale, high-energy physics experiments. Furthermore, MCPs are a critical component in the image intensifiers used by the military and law enforcement as well as in scientific research.

Despite the potential uses for MCPs, existing manufacturing processes are very expensive and this has limited their widespread adoption, especially in applications that require large-area detectors.

But now, Argonne researchers are revolutionizing advanced imaging and sensing technologies. They have combined their atomic layer deposition technology with capillary array plate manufacturing. When used together for high-volume manufacturing, the MCP detector fabrication cost can be reduced by a factor of three to five over conventional processes. This new fabrication technology will pave the way for the increased use of MCPs in a wide range of important applications.

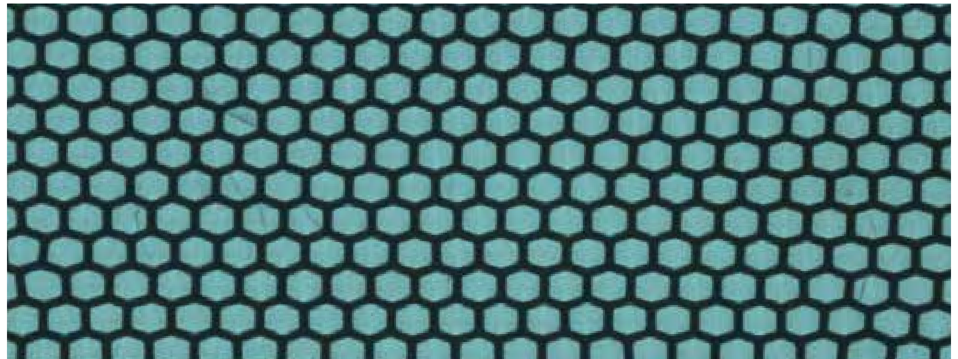


Image shows "honeycomb" structure of a microchannel plate on the micron-scale.

KEY INTELLECTUAL PROPERTY

"Tunable Resistance Coatings," A.U. Mane and J.W. Elam, invention ANL-IN-12-010, (2012). Patent Applications: 13/525,067 filed June 15, 2012 and 13/840,660 filed March 14, 2013.

"Resistive Spacers for Large Area Photodetectors," J.W. Elam, A.U. Mane, H.J. Frisch and R. Northrup, invention ANL- IN-11-070, (2011).

"Microchannel Plate Detectors and Methods for Their Fabrication," A.U. Mane, Q. Peng and J.W. Elam, invention ANL-IN-10-029, U.S. Patent Application 13/011,645 filed January 21, 2011.

"Micro-channel Plate Detector," J.W. Elam, H.H. Wang, M.J. Pellin, K. Byrum and H.J. Frisch, invention ANL-IN-09-017, (2009), U.S. Patent Application 13/032,395 filed February 22, 2011.

Nanocomposite Charge Drain Coatings Eliminate Electrostatic Charge

Argonne scientists are particularly adept at providing new materials solutions to solve performance problems that may occur during development of devices and technologies. In one such case, nanocomposite charge drain coatings were created for uniform deposition over the large, complex 3D surface of a digital pattern generator chip; this eliminates electrostatic charging in ion- and electron-optical devices used by science and industry.

Argonne's coatings are applied using atomic layer deposition, a layer-by-layer thin film deposition technique already used in high-volume semiconductor manufacturing. Unique in composition and nanostructure, Argonne's cost-effective nanocomposite coatings provide unrivaled stability over a wide range of operating conditions and under very high electric fields.

Other potential applications for the thin film coatings are mass spectrometers and surface analysis tools, electron microscopes and conducting spacers.

2013 R&D 100 Award Winner

Device components treated using Argonne Nanocomposite Charge Drain Coatings.

KEY INTELLECTUAL PROPERTY

"Nanoengineered charge drain coating for electron-optical MEMS," J.W. Elam, A.U. Mane, W.M. Tong and A.D. Brodie, invention ANL-IN-13-006, (2013).

"Tunable Resistance Coatings," J.W. Elam and A.U. Mane, invention ANL-IN-12-010, U.S. Patent Application 13/525,067 filed June 15, 2012 and U.S. Patent Application 13/804,660 filed March 14, 2013.

Sequential Infiltration Synthesis Lithography Enables Next-generation Microelectronics

Sequential Infiltration Synthesis (SIS) is a new way of creating nanoscale patterns for microelectronics manufacturing that will reduce cost and enable increased product performance.

Useful for a number of different applications including the creation of semiconducting computer chips and magnetic recording devices, lithography typically refers to the method of using light or electrons to pattern a material. These patterns are traced into a polymer material called a "resist" and are then transferred to the corresponding regions of the underlying material.

On their own, resists typically degrade quickly and are too fragile to allow the patterning of tiny features demanded in the next generation of chips. This physical limitation threatens to halt the nearly 40-year trend of increased performance in microelectronics.

Argonne's SIS technology infuses robust ceramic materials directly into the resist, rendering it up to 100 times stronger. The ability to create sharper lithographic patterns will enable the manufacturing of smaller features (sub 10-nm) in semiconductor devices. Implementation of SIS lithography into existing manufacturing will allow the increased performance trend for microelectronics to continue through at least 2022.

2014 R&D 100 Award Winner

Silicon wafers, ranging in size from 4" to 12" diameter, which have been treated using SIS lithography.

KEY INTELLECTUAL PROPERTY

"Sequential Infiltration Synthesis for Advanced Lithography," S. Darling, Y.-C. Tseng, J.W. Elam and Q. Peng, invention ANL-IN-10-106, U.S. Patent Application 13/427,619 filed March 22, 2011.

"Ordered Nanoscale Domains by Infiltration of Block Copolymers," S. Darling, Y.-C. Tseng, J.W. Elam and Q. Peng, invention ANL-IN-10-017, U.S. Patent Application 13/209,190 filed August 12, 2011.

"Sequential Infiltration Synthesis for Enhancing Multiple-Patterning Lithography," S. Darling, J.W. Elam and Y.-C. Tseng, invention ANL-IN-12-107, (continuous) U.S. Patent Application 13/902,169 filed May 24, 2013.

Ultra-thin Coatings Maintain High Catalyst Activity and Stability

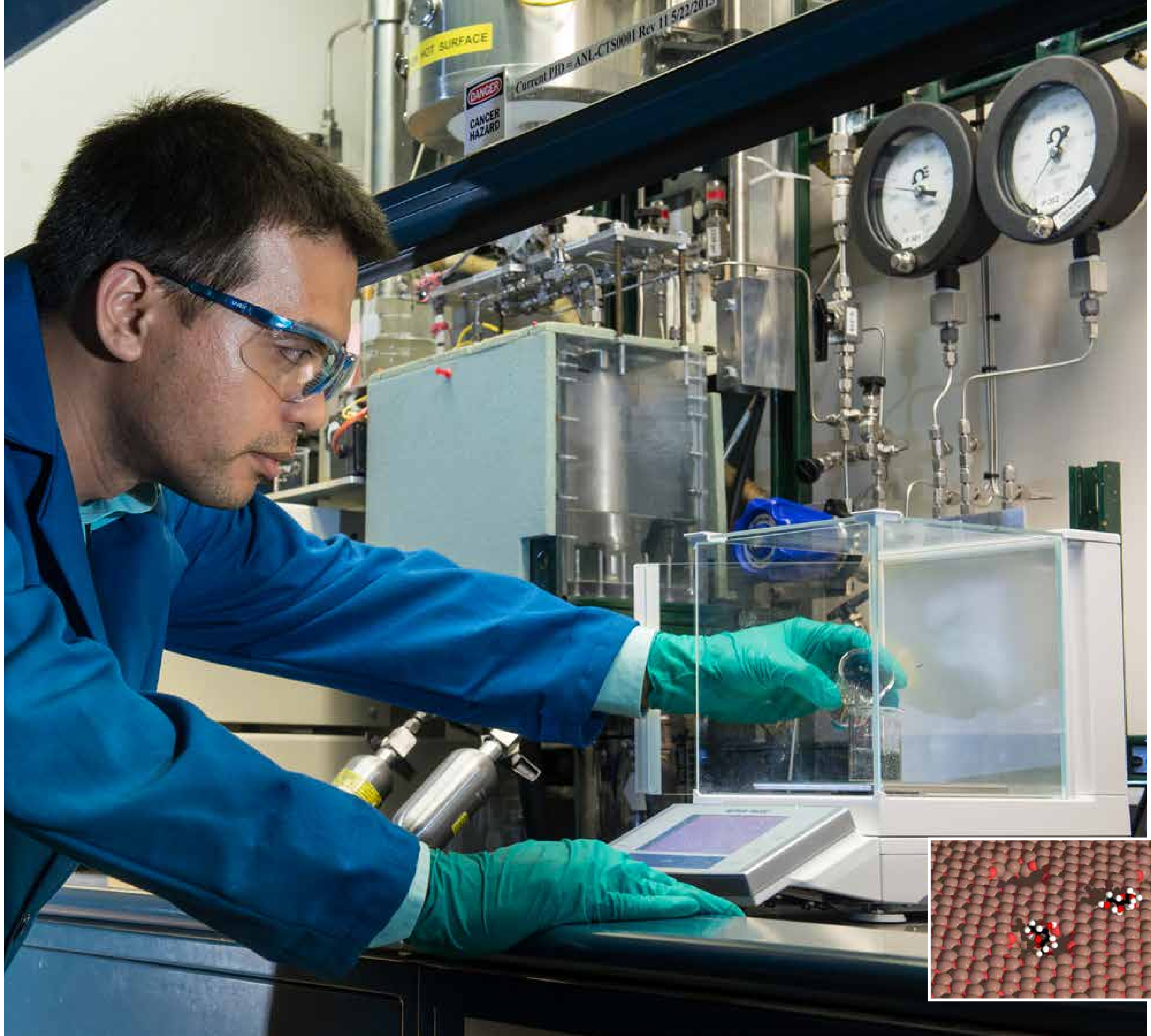
Catalysts are vitally important substances that enable the production of everything from gasoline to fertilizer. However, a number of common chemical and physical catalyst deactivation processes can lead to chemical reactor shutdowns and cause costly manufacturing plant interruptions.

For instance, industrial catalysts comprising noble metal nanoparticles anchored to an inorganic support are prone to deactivate through sintering—at elevated temperatures, the noble metal atoms or particles can diffuse along the support surface and gather into much larger particles having reduced activity. Although a variety of strategies have been developed to inhibit sintering, these methods achieve greater stability at the expense of reduced catalytic activity.

To overcome this, scientists at Argonne are applying ultra-thin protective layers to the catalyst using atomic layer deposition; this reduces sintering and maintains high catalyst activity in high-temperature applications.

In another application of ALD, Argonne researchers worked to improve the efficiency of fuel production from biomass. They created "nanobowls"—nanosized bowl shapes that allow inorganic catalysts to operate selectively on particular molecules. For this application, oxygen can selectively be removed without breaking carbon–carbon bonds.

Argonne's researchers are extending this process to other supported nanoparticle catalysts and ALD coating materials.



Argonne postdoctoral researcher Christian Canlas weighs a catalyst sample in preparation for testing.

KEY INTELLECTUAL PROPERTY

"Improved Hydrothermal Performance of Catalyst Supports," J.W. Elam, C. Marshall, J.A. Libera, J. Dumesic and Y. Pagan-Torres, invention ANL-IN-09-085, U.S. Patent 12/841,805 filed July 22, 2010.

"Subnanometer and Nanometer Catalysts, Method for Preparing Size-Selected Catalysts," S. Vajda, M.J. Pellin, C. Marshall, J.W. Elam and R. Winans, invention ANL-IN-07-067, U.S. Patent 8,148,293 issued April 3, 2012.

"Artificial Zeolites," J.W. Elam and C.P. Canlas, invention ANL-IN-14-069, (to be filed).

"Catalyst and Systems Incorporating the Catalyst," J.W. Elam, M.J. Pellin, J.A. Libera, P.C. Stair, G. Zajac and S. Cohen, invention ANL-IN-07-036, U.S. Patent 7,972,569 issued July 5, 2011.

"Method of Preparing Size-Selected Metal Clusters," J.W. Elam, M.J. Pellin and P.C. Stair, invention ANL-IN-05-0116, U.S. Patent 7,713,907 issued May 11, 2010.

"Catalytic Nanoporous Membranes," M.J. Pellin, J.W. Elam and J. Hryn, invention ANL-IN-03-055, U.S. Patent 7,625,840, issued December 1, 2009.

Calculated structure of fructose molecules adsorbed in nanobowl array.

Thin Films Open Up New Opportunities for Advanced Photovoltaics

Transparent conducting oxide (TCO) thin films are optically transparent and electrically conductive; they play an important role in devices such as solar cells, flat-panel displays and touch screens.

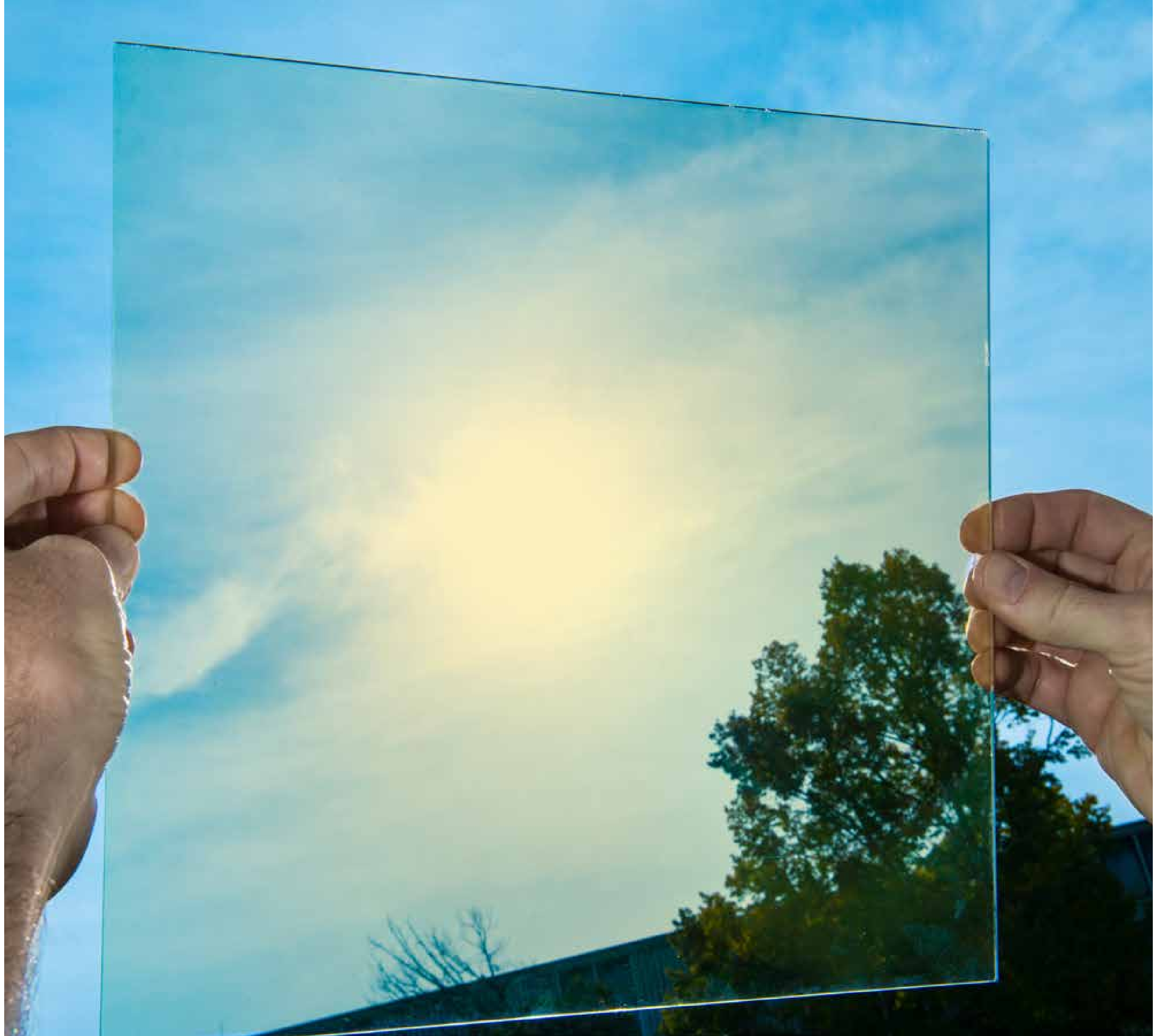
Indium-tin oxide (ITO) is one of the most widely used TCO materials due to its exceptional properties, which include low resistivity. However, limitations in current thin film deposition technology and the high cost of indium are barriers to the deployment of ITO for many applications.

Argonne's vision is to open up new opportunities for next-generation photovoltaic devices by precisely depositing transparent conducting oxide thin films onto nanostructured supports.

To that end, Argonne scientists have invented new atomic layer deposition methods for synthesizing thin films of indium oxide, the major ingredient of ITO. These methods provide numerous advantages over existing thin film technologies including lower deposition temperatures, precise coatings on nanoporous materials, excellent thickness uniformity over large substrate areas and sub-1 nm surface roughness.

This could enable higher energy conversion efficiencies in photovoltaic devices, reduced manufacturing costs, and ultimately, lower costs for producing power.

Ongoing work at Argonne focuses on optimizing ITO material properties and performance, scaling up deposition to larger substrate sizes and applying this material to prototype photovoltaic devices for evaluation and testing.



KEY INTELLECTUAL PROPERTY

"Method for Producing Highly Conformal Transparent Conducting Oxide Films," A.U. Mane and J.W. Elam, ANL-IN-11-042, U.S. Patent Application US 13/249,864, filed September 30, 2011.

"Improved Method for Depositing Transparent Conducting Oxides," J.W. Elam and J.A. Libera, ANL-IN-09-080, U.S. Patent Application US 12/865,305, filed September 30, 2010.

"Synthesis of Transparent Conducting Oxide Coatings," J.W. Elam, A. Martinson, M.J. Pellin and J. Hupp (Northwestern University), invention ANL-IN-06-076, U.S. Patent 7,709,056, issued May 4, 2010.

12" square glass panel coated with ALD transparent conducting thin film.

Working with Argonne

Argonne National Laboratory seeks solutions to pressing national problems in science and technology. The nation's first national laboratory, Argonne conducts leading-edge basic and applied scientific research in virtually every scientific discipline. Argonne researchers work closely with researchers from hundreds of companies, universities, and federal, state and municipal agencies to help them solve their specific problems, advance America's scientific leadership and prepare the nation for a better future. With employees from more than 60 nations, Argonne is managed by UChicago Argonne, LLC, for the U.S. Department of Energy's Office of Science.

For industry inquiries about working with Argonne and the availability of Argonne technologies, please contact:

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